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(71) Applicant: NEOKISMET L.L.C. [US/US]; Suite 1350, 456 Montgomery Street, San Francisco, CA 94104 (US).

(72) Inventors: ZUPPERO, Anthony, C.; 2631 Buena Terra, Pollock Pines, CA 95726-9456 (US). GIDWANI, Jawahar, M.; 2335 Leavenworth, San Francisco, CA 94133 (US).

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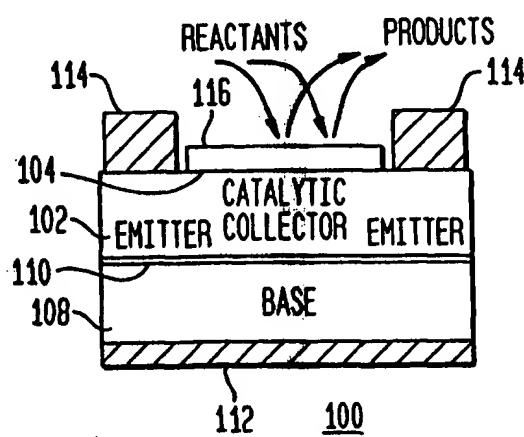
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(54) Title: SOLID STATE SURFACE CATALYSIS REACTOR



(57) Abstract: A method and apparatus to stimulate chemical reactions on a catalyst surface (116) using electricity, and the reverse process to convert energy released from chemical reactions into electricity. A reversible emitter (102) generates electrons which are injected into reactants on the catalyst surface (116), exciting chemically reactive vibrational resonances. Hot electrons created in the emitter region of a semiconductor junction (110) diffuse to the co-located collector region and catalyst surface (116). Catalyst clusters or films bonded on the collector surface transfer the hot electrons to or from the catalyst surface (116) having adsorbed reactants. The dimension of the catalyst-collector (104) is less than the energy mean free path of hot electrons. The hot electrons excite reactant vibrations before thermalizing with the substrate lattice thereby accelerating reactions. The hot electrons are also generated by the same reactions on a catalyst surface. The method and apparatus is reversible and may be operated as an electric generator using chemical reactions.

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SOLID STATE SURFACE CATALYSIS REACTOR

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## TECHNICAL FIELD OF THE INVENTION

The present invention relates generally to an energy generator and more specifically to a method and apparatus to couple the excitation structure of a semiconductor substrate to the excitation structure of reactive adsorbates on the surface of a catalyst.

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## BACKGROUND OF THE INVENTION

Recent experimental and theoretical developments in surface science showed how hot electrons cause heating of the vibration of molecules or atoms adsorbed on a catalyst surface. The energy of hot electrons is defined as electrons with effective temperatures between 600 Kelvin and 60,000 Kelvin, which means equivalent energies between 0.05 and approximately 5 eV, or many times that of thermal energy at room temperature. 300 degrees Kelvin is 0.026 eV.

It has been discovered that hot electrons that diffuse to a catalyst metal surface interact strongly with the adsorbed surface chemicals, also called adsorbates, and can do so at a rate faster than the process of electrons thermalizing with the lattice of catalyst metal atoms. It has also been recently discovered that the adsorbates acquire vibrational energy when interacting with hot electrons from the catalyst surface. It has been further discovered that adsorbate vibrational energy strongly enhances the rate of chemical reactions, and in some cases enable reactions that do not occur by thermal means because of the activation energies or chemical thermodynamics involved. Hot electrons stimulate adsorbate chemical reactions on a catalyst surface. The reverse of this process has also been observed, where a surface chemical reaction resulted in the production of hot electrons.

The presence of hot electrons on the surface of the catalyst can cause a pseudo-thermal regime in which the surface vibrations of adsorbate molecules, either against themselves or against the catalyst, are in equilibrium with the temperature of the substrate hot electrons rather than with the physical temperature of the substrate itself. This means the vibrations can be at several thousand degrees while the catalyst is at ambient temperature. Hot electrons excite the adsorbate from the bottom of its adsorption well in a stepwise manner, and may even do so until it overcomes the adsorption barrier and hops to a neighboring potential well, reacts or desorbs.

The hot electron energy or frequency need not exactly match that of the adsorbates. The adsorbate excitation structure is generally very broad, being spread over many frequencies, and the mechanism is often via an electronic excited state. That is, when the adsorbate acquires an electron it transitions to an excited electronic state. Within a few tens of femtoseconds it begins to move outward away from the surface, and then releases the electron. The adsorbate now transitions back to a non-electronic excited state. However, it retains the extra energy given to it by the hot electron. As a result, the adsorbate is in a higher vibration state. The tens of femtosecond lifetime for the process causes a broadband resonance feature and hence permits an energy mismatch between hot electron and the receiving adsorbate energy levels. The substrate electron in effect deposits energy into a vibration mode of adsorbate reactant, such as the vibration of the atoms in the adsorbate reactant molecule or in the vibration of the adsorbate against the catalyst surface. This process can repeat itself many times, to the point where the adsorbate desorbs. In the literature this is called "Desorption Induced by (Multiple) Electronic Transitions," Abbreviated DIMET or DIET. This is the stimulator process.

The generator process works in reverse. An adsorbate with energy in one of its vibration modes attracts and acquires a cold electron from the catalyst. This causes a transition where the adsorbate with 5 attached electron then becomes a charged adsorbate specie in an excited electron state. Within femtoseconds this specie in the excited electron state decays and ejects an electron. This leaves the adsorbate reactant with less energy in its vibration 10 mode and the electron with excess kinetic energy. The effect is that the energetically excited reactant on the surface of the catalyst gave a fraction of its energy to an electron in the catalyst. This is the generator process.

15 This generator or reverse process has been observed in laboratories. The detector in this observation used a short circuit Schottky diode to measure an electron flux directly generated by the surface reactions. The laboratory detector measured a current in a short 20 circuit diode, which means the detector generated almost exactly zero power. However, the detector confirmed the existence of the generator mode. Both hot electrons and hot holes were observed, and with energies in excess of the Schottky barrier in silicon, which is of order 0.5 25 eV.

Hot electrons on a catalyst surface have been shown to accelerate reactions. Experiments with vibrationally excited Nitrogen Oxide (NO) molecules interacting with a copper (Cu) surface showed thousand-fold enhancement of 30 surface reactivity. Up to near unit reaction probability was observed. In that work, neither reactant translational energy nor surface temperature had a strong effect on the reaction probability, confirming the efficacy of using hot electrons.

35 In another experiment, carbon monoxide (CO) was oxidized on a ruthenium surface. A 1.5 eV, 110 femtosecond laser pulse duration created the hot electrons. It was observed that sub-picosecond

reactions of adsorbed O with CO to produce CO<sub>2</sub> in a reaction that is energetically not possible at all without the hot electrons. This means if one uses thermal energy alone, CO will desorb without reacting.

5 The efficiency of such hot electrons to impart vibrational energy to just the adsorbates can approach 100%. Nearly 100% desorption of CO from a copper surface was observed. A three order of magnitude increase in reaction rate of NO with Cu was also  
10 observed.

This establishes the strong, two way energy transfer between hot electrons and excited adsorbate specie on a metal catalyst surface. The collection of observations leads to both an apparatus and method to  
15 couple the excitation structures of the adsorbate reactants adsorbed, chemisorbed or physisorbed on a catalyst surface to the excitation structure of a semiconductor diode in close proximity to the adsorbates.

20 The semiconductor diode excitation structure is rather simple, consisting of holes in the valence band and electrons in the conduction band. The excitation structure of the chemically reactive adsorbate-catalyst system is dominated by vibrations of the atoms and  
25 molecules with themselves and against the substrate, forming energy level bands, and the energy level bands due to electronic excited states of these specie, where the adsorbates may acquire a transient or permanent charge.

30 Coupling of these structures occurs mainly by two paths, either directly through the direct, typically ballistic transport of the hot carriers such as hot electrons or hot holes, between adsorbate and semiconductor, or by resonant tunneling of energy.

35 Resonant tunneling couples the two structures through oscillating electric fields produced by the excitation structures in the semiconductor and adsorbate-catalyst system. The coupling is greatly enhanced when the

frequencies of the excitations on either side are close to each other.

Hot electrons are the easiest excitation to work with. The current method of choice to produce and 5 inject the hot electrons into a metal catalyst surface relies on a pulsed laser. The usual method to produce these hot electrons is to irradiate the surface of the metal with a short laser pulse, typically with pulse duration in the range of 50 to 1000 femtoseconds and 10 with photon energies of 1 eV or greater (0.2 to 1.5 micron wavelength). The photons are adsorbed and produce electrons with energies between 0 eV and up to the photon energy, splitting the energy with a hot hole, and with hot electron energies averaging approximately 15 half the incident photon energy. A laser, however, is one of the most expensive energy sources available.

A theory to use a solid state metal-insulator-metal junctions to produce resonantly coupled, hot electrons has been proposed. The theoretical suggestion would 20 produce resonance-assisted, hot-electron-induced femtochemical processing at surfaces. The energies relative to the catalyst Fermi level and associated with the metal-insulator junctions is higher than what is now known to be appropriate for surface resonances. No 25 experiments using this theory are known at this time. No known mention of process reversibility has been claimed.

The use of a neutral semiconductor substrate as the injection mechanism into thin metal overayers, with 30 photons derived from a pulsed laser as the creator of hot carriers in the semiconductor, was also suggested in the literature. It was suggested that this could be an order of magnitude more efficient for stimulating gas-surface catalytic reactions than using the metal as the 35 photon acceptor. It was suggested that using a semiconductor substrate, metal overlayer and catalyst device to produce hot electrons more efficiently with photons and inject them into a catalyst surface. A

critical detail needed to render the process efficiency useful was not addressed in a way needed to assure process efficiency. One must tailor the Schottky junction, the ohmic junction or the almost ohmic junction between the semiconductor and the metal so that the coupling of either hot carriers such as hot electrons or holes is electrically efficient, or so that the resonant tunneling is efficient. The proper use of resonant tunneling and resonance-assisted processes can be valuable components in a useful device and method.

A Schottky junction diode has been used in experiments for hot electron injection into solutions. One of the co-authors of that work suggests that they did not achieve the success they wanted because the surface states associated with the electrolyte cooled the electrons. A catalyst electrode Schottky junction made of n-silicon and platinum metal was used to inject electrons into a reactive electrolyte solution. The platinum thickness was varied from less than the mean free path to several times thicker than the mean free path of hot electrons in platinum. They achieved some success, and also suffered severe problems with interactions between hot electrons and electrolyte. Flooding the surface with liquid electrolyte destroys the effectiveness of hot electrons. Metal-oxide junction surface states have been an unsolved problem with this approach, where liquids flood the reactive surface.

It is now known that outer layers, away from the catalyst surface, of multiple layers of adsorbates that accumulate on the metal-liquid interface trap hot electrons as "polaritons" and render them less useful as a source of prompt reaction stimulators or as generators of excitations. The efficacy of a semiconductor substrate under a metal and catalyst reactive surface is a valuable element. A semiconductor diode is a critical element.

Implicit in all the observations is the efficiency of pulsed operation. In the case of a reaction

stimulator, the duration of the pulses generating hot electrons is less than the time associated with electron thermalization with the lattice. In the case of a generator, the sudden burst of chemical reactions causes 5 a flood of hot electrons on the catalyst surface. This in turn causes a flood of electrons in the conduction band of the semiconductor substrate collecting those hot electrons. A sufficiently short burst causes the number of generated electrons to exceed the thermally occurring 10 short circuit electrons, thereby increasing the efficiency of the generation of electricity.

Missing in the public domain are methods to tailor the surface of the catalyst to enhance resonant tunneling, to enhance the activation of selected energy 15 bands, to enhance the probability of desired energy transitions, or to enhance the selected reaction pathways.

#### SUMMARY OF THE INVENTION

20 The present invention is directed to a method and apparatus to couple the excitation structure of a semiconductor substrate to the excitation structure of reactive adsorbates on the surface of a catalyst. Preferably, the coupling is reversible. The reversible 25 reactor uses excitations originating in a semiconductor substrate to stimulate chemical reactions by the adsorbate species on the surface of a catalyst, and uses the reverse process to generate excitations in the substrate as the result of reactions. The method and 30 apparatus when operated in the stimulator mode uses electrical or other forms of energy input to the semiconductor substrate to manipulate the reaction path so as to accelerate reactions, to steer the reactions, to manipulate the forms of energy produced by the 35 reaction, and to reduce the temperature needed to stimulate surface catalytic reactions; when operated in the generator mode the apparatus converts excitation energy of the adsorbate-catalyst system into electricity

or other forms of energy in the semiconductor substrate; and when operated in the stimulator-generator mode, may use electricity or other forms of energy to manipulate reactions and at the same time may generate electricity 5 or other forms of energy from the adsorbate-catalyst system chemical reaction energy.

In the present invention, electricity or other forms of energy are used to create and inject excitation energy, such as hot carriers, into adsorbates on a 10 catalyst surface and to stimulate adsorbate-surface catalytic reactions; and, because of the reversible nature of the process, one and the same type of apparatus may also be directed to collecting excitations that result from surface chemical reactions, such as hot 15 carriers in a semiconductor substrate, and converting them into electricity or other forms of energy. In an exemplary embodiment, the present invention uses electronically energized semiconductor diodes in a novel way to stimulate the reactions. For example, in one 20 embodiment, the present invention utilizes a p-n junction as the creator of hot carriers and as the injection mechanism to couple them into thin metal overlayer structures of catalyst material and to adsorbates on the catalyst surface. The same embodiment 25 may use the same p-n junction to collect hot carriers in the semiconductor diode, forward biasing it and hence generating electricity.

The present invention includes a hot carrier emitter, also known as an excitation emitter, in 30 intimate contact with a catalyst ensemble energy collector also known as a catalytic collector. The excitation emitter includes a semiconductor diode.

When the apparatus is operated in the stimulator mode, electrical or other energy input to the 35 semiconductor diode causes it to generate excitations such as an excess of holes or electrons, and the resulting hot carriers and resonantly coupled excitation energy is coupled to and absorbed by the excitation

structure of a catalyst-adsorbate system, thereby stimulating adsorbate chemical reactions.

When the apparatus is operated in the generator mode, excitation energy originating in a catalyst-  
5 adsorbate system is coupled into semiconductor band excitations, which can typically cause a forward bias in the semiconductor and generate electricity or other useful forms of energy.

The semiconductor diode includes an emitter, a  
10 diode junction and a semiconductor base. The emitter, which is in intimate contact with the catalytic collector, includes a semiconductor when the diode is a p-n junction diode, or the emitter includes a metal when the diode is a Schottky diode. The junction is the  
15 region of contact between the emitter and the base. The emitter also includes an electrical contact. When the hot carrier, semiconductor excitation, is chosen to be an electron then the base includes an n-type semiconductor and the emitter includes either p type  
20 semiconductor or a metal. When the hot carrier is chosen to be a hole, the base includes p type semiconductor and the emitter includes either n type semiconductor or a metal. The base also includes an electrical contact.

25 The catalytic collector is placed in intimate contact with the emitter and includes a catalyst, an optional underlayer, and optional reaction accelerator-decelerator materials. Elements of the catalytic collector may be one and the same with elements of the  
30 emitter. A surface of the catalyst and of the optional reaction accelerator-decelerator materials comes in intimate contact with the reactant chemicals.

Various regions of a device using this invention may include various and different catalytic collectors, 35 hot carrier emitters and various modes of energy coupling, including ballistic transport and resonant tunneling.

Further features and advantages of the present invention as well as the structure and operation of various embodiments of the present invention are described in detail below with reference to the 5 accompanying drawings. In the drawings, like reference numbers indicate identical or functionally similar elements.

#### BRIEF DESCRIPTION OF THE DRAWINGS

10 Preferred embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings in which:

15 Figure 1 shows a general schematic cross section of a solid state surface catalysis reactor device of the present invention in one embodiment;

Figure 2 illustrates a cross section of a catalytic collector in one embodiment of the present invention;

20 Figure 3 shows a cross section of a reaction stimulator device with catalyst clusters forming the catalytic collector;

25 Figure 4 shows a cross section of a solid state surface catalysis reactor device with a thin electrode forming a substrate for catalyst clusters as part of a catalytic collector and also forming the electrical connection for the hot carrier emitter;

Figure 5 illustrates a cross section of a solid state surface catalysis reactor with reaction accelerator-decelerator materials surrounding or adjacent to catalyst metal;

30 Figure 6 illustrates a cross section of the solid state surface catalysis reactor having a single metal element that is at the same time an electrical connection to the emitter, the underlayer of the catalytic collector and forming the metal element of a 35 Schottky diode; and

Figure 7 shows the electronic energy level diagram for the a solid state surface catalysis reactor,

illustrating the regions from the  $n+n$  type base to the adsorbate.

## DETAILED DESCRIPTION OF THE

## PREFERRED EMBODIMENT OF THE INVENTION

An exemplary embodiment of the present invention uses electrons as the hot carriers and a p-n junction diode as the semiconductor diode. The base is n type semiconductor and the emitter is an p type semiconductor. A forward bias on the p-n junction diode injects minority carrier electrons into the conduction band of the p type emitter where they become minority carriers. The minority carriers diffuse and migrate to the catalytic collector and may also be resonantly coupled into the excitation structure of the adsorbate-catalyst system provided that the distance from the junction to the catalytic collector is less than several times the diffusion length of minority carriers in the p type semiconductor. For example, when InSb, InAs, or some alloy of InGaAsSb is the semiconductor, then the diffusion length can range from approximately 100 nanometers to several microns.

According to this invention, the minority carrier electrons are injected or resonantly coupled into the catalytic collector with an energy in excess of the Fermi level of the catalytic collector. This excess energy is nearly mono-energetic and has a value approximately equal to the forward bias on the diode. When the semiconductor is a p-n junction diode, the minority carrier energy may be within approximately several  $kT$  of the semiconductor band gap energy ( $kT$  = thermal energy, 0.026 eV). When the semiconductor diode is a Schottky junction the carrier energy may be within approximately several  $kT$  of the energy needed to overcome the Schottky barrier. The electrons with forward bias energy, also called hot electrons, may rapidly permeate on to a surface of the catalyst facing and in intimate contact with reactants if, for example,

the distance from the p type semiconductor to the surface in contact with the reactants is less than the several times the energy mean free path of electrons in the catalytic collector.

5 When the catalyst is a metal such as platinum, palladium, rhodium or ruthenium the energy mean free path ranges between 5 and 50 nanometers. When the underlayer is copper or gold the energy mean free path ranges between 50 and 200 nanometers.

10 The flux of hot electrons interacting with the reactant chemicals is approximately that of the diode forward current if the distance from the catalytic collector to the diode junction is within the diffusion length of the emitter semiconductor and energy mean free  
15 path lengths of the catalyst and underlayer, as specified herein. Hot electrons interact strongly with adsorbates.

Another aspect of the present invention uses a Schottky diode designed to have a low barrier height, 20 also referred to as a tunneling junction. Such a device is constructed by choosing the doping between the metal and the semiconductor of the Schottky junction to be intermediate between the very high doping used to make an almost ohmic junction, typical for making electrical  
25 contacts with the semiconductor, and the medium doping used to make a normal Schottky diode. The doping controls the width of the depletion region and hence the strength of the Schottky barrier. The value of the doping may be chosen between degenerate or high doping  
30 and conventional or moderate doping, depending on the application.

When the semiconductor is silicon and the metal is any metal associated with the catalytic collector then the doping may be adjusted to an effective value of  
35 order 0.1 eV. High doping in silicon yields effectively 0.0 eV barrier and normal doping yields barriers typically between 0.5 and 1.5 eV barrier. This tunneling junction Schottky diode permits the use of

common semiconductor materials such as silicon. The use of such a diode is appropriate for use in the generator mode where reactions are pulsed.

With the methods and apparatus provided in either 5 the p-n junction diode or the Schottky junction embodiment of the present invention, the semiconductor diode injects hot carriers or resonantly couples the carriers and with energy approximately equal to the energy of the diode forward bias voltage into the 10 adsorbates on a surface of the catalytic collector. With the methods and apparatus provided in this invention, the energy of the injected electrons may be chosen by the user so as to steer reactions and to drive reactions in selected modes or pathways, including 15 reaction paths inaccessible to thermal processes.

Another novel aspect of the present invention is the reversible nature of the present invention. For example, the inverse of the stimulation process is the collection of electrons generated by adsorbates reacting 20 on the catalytic collector and the resonant coupling of energy into the semiconductor diode, creating carriers such as conduction band electrons or valence band holes. The catalytic collector acts like a collector of hot electrons generated by adsorbate chemical reaction 25 energy instead of a collector of hot electrons generated by the hot carrier emitter. The catalytic collector couples excitations from the adsorbates to the semiconductor, instead of from the semiconductor to the adsorbates. The hot carrier emitter gets its hot 30 electrons from the catalytic collector instead of from the diode junction. The hot carrier emitter may generate its electrons by resonant coupling of energy from the excitation structure of the adsorbate-catalyst system. The hot electrons go into the diode junction 35 towards the base instead of out of the diode junction from the base. In so doing, the hot electrons maintain a forward bias on the diode, thereby generating electricity. This reversible nature of the present

invention permits the device to generate electricity as a direct result of chemical reactions. This is a generator mode.

This same device may operate both in a stimulator and generator mode simultaneously, and thereby generate electricity more efficiently than operation in the generator mode alone. Operated in this way, the stimulator apparatus triggers and stimulates adsorbate reactions by the application of electricity or other forms of energy to the semiconductor diode. This initiates and causes the reactions to complete in a short time, for example, in the order of picoseconds. The burst of reactions result in a high peak power burst of chemical reactions, with concomitant release of electrons. The resulting flood of electrons may then be collected, thereby generating electricity. The resulting electrons may also stimulate more chemical reactions and may initiate a chain reaction analogous to an explosion or detonation. The result is a form of surface explosion. The electrons may then generate electricity much more efficiently in the semiconductor diode. The electric generating efficiency of a diode is a strong function of the peak power, and the stimulator may create a condition where the reactions achieve such high power.

When the device is operated in the stimulator mode, energy may be collected in any manner including by operating the solid state surface catalytic reactor in the generator mode. Other modes of collecting energy include but are not limited to collecting radiations emanating from reactions that have been stimulated, or by collecting heat, or by collecting the reaction products themselves, or by capturing the kinetic energy of the products as they desorb, or by collecting the phonons, or by stimulating and collecting coherent acoustic or optical radiation, or by stimulation of piezoelectric devices.

When the device is operated in the generator mode, stimulation may be achieved in any manner, including by operating the solid state surface catalytic reactor in the generator mode. Other modes of stimulation include 5 but are not limited to stimulation using pulsed laser light, a simple light flash, or the hot carriers generated on other regions of the device by other reactions whose energy outputs may include hot carriers and other catalytic products that stimulate reactions.

10 With the p-n junction semiconductor in the present invention, semiconductors with band gaps starting from approximately 0.05 eV to 5 eV may be used with room temperature heat sink operation, and band gaps less than 0.05 eV may be used when the system is operated at lower 15 than room temperature. This does not preclude using materials with higher bandgaps, such as insulators like CaF<sub>2</sub> with 12 eV bandgap, or any other material with higher bandgap. In particular, the commonly used InSb and InGaAsSb materials have band gaps that may be 20 continuously chosen in the range 0.1 to 1.5 eV by suitable choice of the In / Ga ratio and the As / Sb ratio. The resulting range of band gaps lie precisely in the range of energies associated with hydrocarbon chemical bonds. The InSb material produces 0.18 eV 25 electrons, which is ideal for favoring reaction stimulation Vs desorption, because higher energy electrons may stimulate an undesirable large fraction of desorptions, as opposed to surface reactions.

30 The p-n junction embodiment of this invention provides a substrate whose energy levels match the excited state energy levels of the adsorbates. This greatly enhances resonant transfers, in either direction, that is, to or from the adsorbate. The metals of the catalytic collector provide a resonant 35 tunneling coupling, for example, via plasmons, between the adsorbate and the semiconductor substrate. The resonant tunneling coupling effectively connects the energy band structure of the substrate to the energy

band structure of the adsorbates. An ohmic or almost ohmic junction between the catalytic collector and the semiconductor effectively pins the Fermi level of the catalytic collector to the valence band of the 5 semiconductor. The conduction band of the semiconductor, being higher than the valence band by an amount equal to the band gap of the semiconductor, then appears above the Fermi level of the catalytic collector by the same amount, namely the band gap energy. Since 10 the bandgap may be chosen from a palate between 0.05 to 5 eV, the bandgap energy may be made to match nearly any energy level of the system having the adsorbate and the catalytic collector. By choosing the semiconductor band gap to match the energy level of an adsorbate on the 15 catalytic collector, one may effectively couple the two together through the well known and commonly used process of resonant tunneling. Resonant tunneling greatly increases the cross section for the transfer of energy.

20 This is useful in the stimulator mode to steer reactions because selected energy levels of the adsorbate may be resonantly activated by hot carriers coming from the semiconductor. This is useful in the generator mode because excited vibration states of 25 adsorbates may be coupled resonantly to the semiconductor, enhancing energy transfer. This is useful in the stimulator-generator mode because the stimulator can trigger and initiate adsorbate reactions, using a relatively small stimulator energy, and the 30 reactions may then spread in a manner analogous to an explosion or detonation on the surface catalytic collector exposed to reactants, which release hot carriers. The hot carriers may then generate electricity at a rate faster than they loose energy by 35 generating heat.

In one embodiment, hot carrier emitters are fabricated using degeneratively doped or highly doped p-n junctions. In this embodiment, the switching speed

can approach that of the Schottky junction because of the high carrier densities, and also because the high semiconductor doping densities form abrupt junctions, similar to that of a Schottky diode. High switching speed enhances the ability to pulse the stimulator and cause high peak power reactions. Next, the p-n junction may provide lower energy hot carriers, as low as 0.05 eV and certainly below 0.4 eV, and determined by the chosen bandgap. The p-n junction may provide very high energy monochromatic hot carriers, with energies equal to the semiconductor band gap, which exceed 5 eV for known devices. The p-n junction provides a much longer diffusion dimension than that of the Schottky junction, between 200 nanometers and several microns, over which the hot carrier can migrate and interact with surface catalysts, permitting much larger and manufacturable semiconductor devices. Further, highly doped or degeneratively doped semiconductor junctions may be produced with nearly ohmic contacts, mitigating the surface state problems.

Another novel aspect of the present invention is the co-location of both an electrically powered reaction stimulator and its inverse, a reaction driven electric generator. The stimulation causes a high rate of reaction, resulting in high peak power which in turn makes the energy generator more efficient.

In another novel aspect, the present invention allows the device to act as both stimulator and generator. The uses of combined reaction stimulation include: 1) controlling catalytic reactions; 2) monitoring those reactions using the generated electrical signal; 3) accelerating reactions on catalysts that have undesirable slow reaction rates but highly desirable selectivity; 4) causing non-thermal steering of reaction paths; 5) stimulating extremely rapid surface chain reactions to achieve high peak power while maintaining low average power; 6) causing chemical reaction temperatures like that of the hot carriers in

the catalyst, which may be far in excess of the catalyst physical temperature; 7) in the stimulator-generator mode, using one type of stimulator to pulse the device to make electricity and another type to cause a self 5 cleaning of the device, for example to remove unwanted chemical byproduct that may build up and accumulate with use, 8) initiating reaction avalanches such that the chemical reactions create their own hot carriers, forcing hot carriers to diffuse in the reverse 10 direction, and causing the device to be an electric generator.

As described hereinabove, the present invention is directed to various aspects of the methods and devices that stimulate and manipulate chemical reactions using 15 electrical energy input on selected catalyst surfaces, and that produce electrical energy through an inverse process.

For example, the present invention is directed to a method and apparatus for making a device that will 20 generate hot carriers, especially hot electrons, transport them and couple them to reactant adsorbates on a catalyst surface and cause such adsorbates to acquire an effective vibrational temperature in excess of the temperature of the catalytic surface. Vibrational energy 25 and temperature are used interchangeably. Energy is the product of the Boltzman constant and absolute temperature. Such an effective vibrational temperature in turn accelerates the reaction rates on the catalyst. Excited vibrational states of atomic and molecular 30 adsorbates, both against the catalyst surface and internal to the adsorbates, are observed to be orders of magnitude more reactive than adsorbates in ground states. The methods and apparatus of the present invention increase adsorbate vibrational energy or 35 temperature using an electrical stimulus without appreciably increasing the substrate thermal energy or temperature.

In another aspect, the present invention is directed to methods and apparatus for reversing the above-described process, wherein excitation energies, electrons or holes generated by chemical reactions 5 described herein above are converted coupled into a semiconductor substrate and into electricity.

Accordingly, one aspect of the present invention is directed to a reaction stimulator method and device to use electricity to create energetic carriers, 10 particularly hot electrons, in a hot carrier emitter and inject those carriers efficiently into a catalytic collector. Preferably, the catalyst or substrate temperature need not be raised during the reaction stimulation.

15 In another aspect, the present invention is directed to methods and apparatus for a reaction stimulator - generator that efficiently collects energetic carriers generated by reactions on a catalyst surface, particularly hot electrons, and cause them to 20 charge a forward biased diode through an emitter-base junction, thereby generating electricity.

In another aspect, the present invention is directed to a reaction stimulator that injects hot carriers or hot electrons with the range of energies 25 needed to selectively favor desired types of surface chemical reactions. Preferably, the reaction stimulator is simple in design, rugged in construction, and economical to manufacture.

30 In another aspect, the present invention is directed to a reaction stimulator that is reversible, wherein the diffusion of hot carriers may proceed in either direction, that is, either from a chemical adsorbate reaction to a hot carrier emitter, which generates electricity, or from a hot carrier emitter to 35 a chemical adsorbate, which uses electricity to stimulate reactions.